Enabling Extreme Fast Charging Through Control of Li Deposition Overpotential

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Project ID: bat396

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Overview

Timeline

- Project start date: Jul. 2018
- Project end date: Aug. 2020
- Percent Complete: 35%

Barriers

- Barriers addressed:
  - ➢ The major barrier preventing extreme fast charging of Li-ion batteries is Li plating at the graphite anode.

Budget

- Total project funding:
  - ➢ DOE share: $800,000
  - ➢ Cost share: $82,496
- Funding for FY 2019: $400,000

Partners

- Collaboration: Stony Brook University (SBU) and BNL
- Project Lead: SBU

Relevance

Project Goal

- Demonstration of a Li-ion battery utilizing a surface treated graphite electrode that will enable extreme fast charging by changing the overpotential for lithium deposition.

Impacts

- Surface coatings on a graphite electrode will increase the overpotential for Li nucleation and growth, thus suppressing Li deposition at high charge rates.
- By mitigating Li plating, the battery will address the EERE goal of achieving 500 6C charge/ 1C discharge cycles with less than 20% fade in specific energy delivered from fast charge protocol, while achieving state-of-the-art cell specific energy and cost.
- Deliberate increase of Li deposition overpotential is a new concept – the program represents a potentially transformative strategy for Li plating suppression

Resources

➢ Personnel

Stony Brook University

- Prof. Esther Takeuchi (PI) responsible planning for project reassignment and task reallocation. Lead efforts on systems level assembly, characterization, and testing
- Prof. Kenneth Takeuchi (Co-PI) lead process development efforts
- Prof. Amy Marschilok (Co-PI) lead cell testing and functional characterization efforts
- Graduate student researchers execute data collection and analysis

Brookhaven National Laboratory

- Assistant Scientist David Bock leads electrode characterization efforts

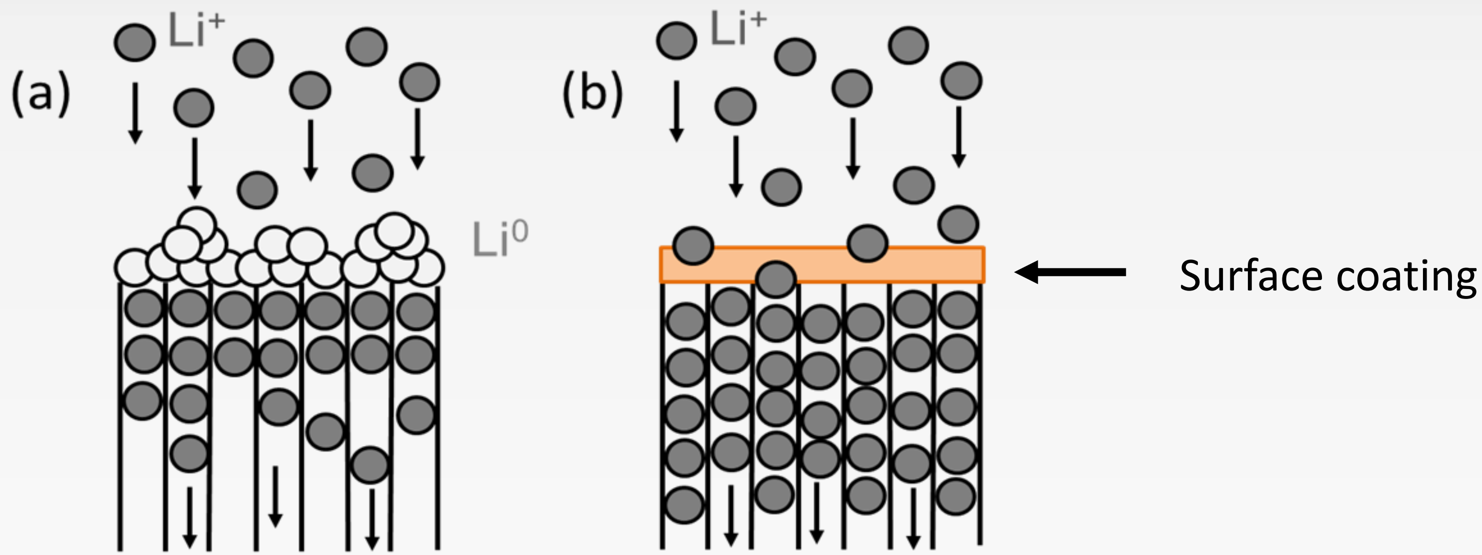
➢ Facilities

Laboratories within Chemistry Department and Advanced Energy Research and Technology Center at SBU and Interdisciplinary Science Building at BNL

- Extensive characterization tools, electrochemical potentiostats, cyclers, ACI
- Center for Functional Nanomaterials at BNL (SEM, AFM, XPS, Sputterer)
- Pouch cell pilot fabrication line

Approach – Concept Summary

- **Concept:** graphite electrodes coated with nanometer scale surface coating



- Deliberate modification of the graphite substrate will increase the overpotential for Li deposition during battery charging.
- Overpotential for Li deposition on the modified electrode surface will be greater in magnitude than the overpotential for intercalation into graphite, resulting in preferred lithiation of graphite and *inhibited* Li plating.

Approach – Control of Li Deposition Overpotential

- During deposition of Li via electrocrystallization, a free energy barrier must be overcome for the formation of Li nuclei on the electrode surface to occur.

- Electrode overpotential during electrocrystallization can be described as:

$$\eta = \eta_n + \eta_p$$

η_n : nucleation overpotential – initial nucleation of Li clusters

η_p : plateau overpotential – continued growth of Li on existing nuclei

- **Surface treatments with materials with high overpotentials unfavorable for Li deposition were selected for the project**.

Approach - Project Objectives

Objective 1: Prepare and characterize graphite electrode modified with surface treatment.

Objective 2: Perform electrochemical evaluation of surface treated graphite electrodes in half and full cell configurations.

Objective 3: Improve cell rate capability and cycle life through optimization of surface coating type and thickness.

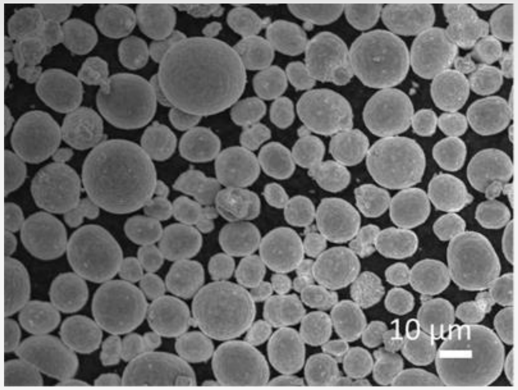
Objective 4: Evaluate extreme fast charging capability of cells containing surface coated graphite electrodes and benchmark against cells using uncoated graphite electrodes.

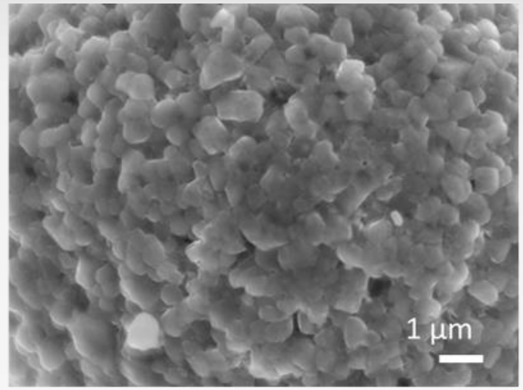
Milestones

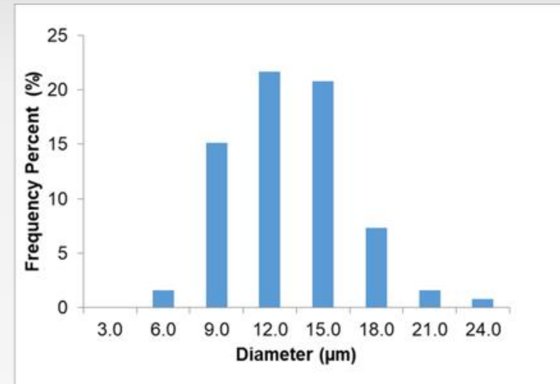
Date	Milestone and Go/No-Go Decisions	Status
Sept. 2018	Characterization of electrode materials	Completed
Dec. 2018	Preparation and characterization of surface treated graphite electrodes at a single nm scale thickness	Completed
Mar. 2019	Determination of functional capacity of surface coated graphite electrodes in half cell configuration	Completed
June 2019	**Go/ No-Go:** Demonstration of full cells utilizing a treated electrode capable of 50 cycles at C/2 charge rate; capacity retention ≥ 80% of control cells	On Track
Aug. 2019	Nine (9) 2 Ah cells incorporating initial fast charge technology provided to DOE	On Track
Sept. 2019	Preparation and characterization of surface coated graphite electrodes at different thicknesses	0% complete
Dec. 2019	Optimization of surface coating type and thickness in full cell configuration	0% complete
Mar. 2020	Identification of surface coated electrode with optimum cycling performance at 3C rate	0% complete
June 2020	Demonstration of surface coated electrode with capacity retention at 6C charge rate > uncoated (control) electrode	0% complete
Aug. 2020	Eighteen (18) 2 Ah cells incorporating final fast charge technology provided to DOE	0% complete

Technical Progress – Electrode Material Characterization

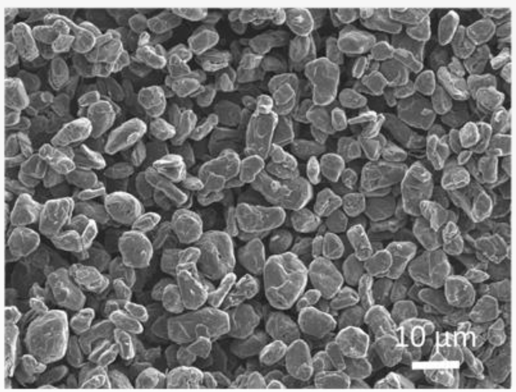
NMC622

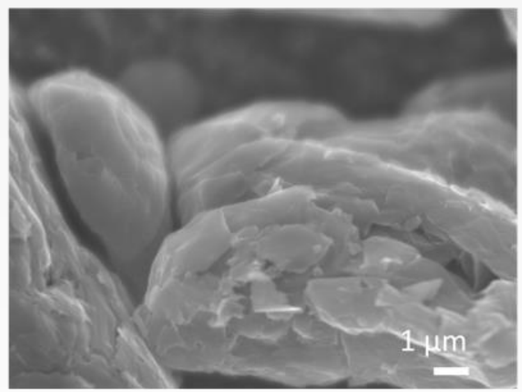


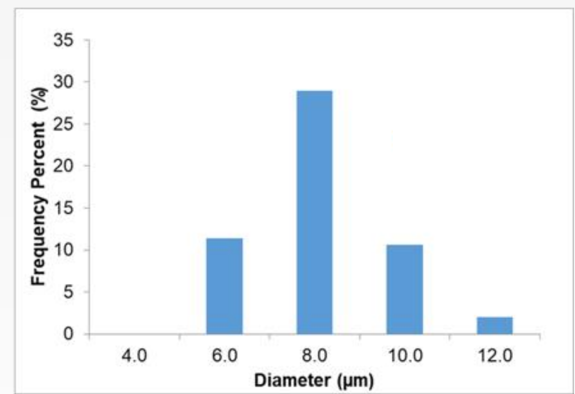




graphite



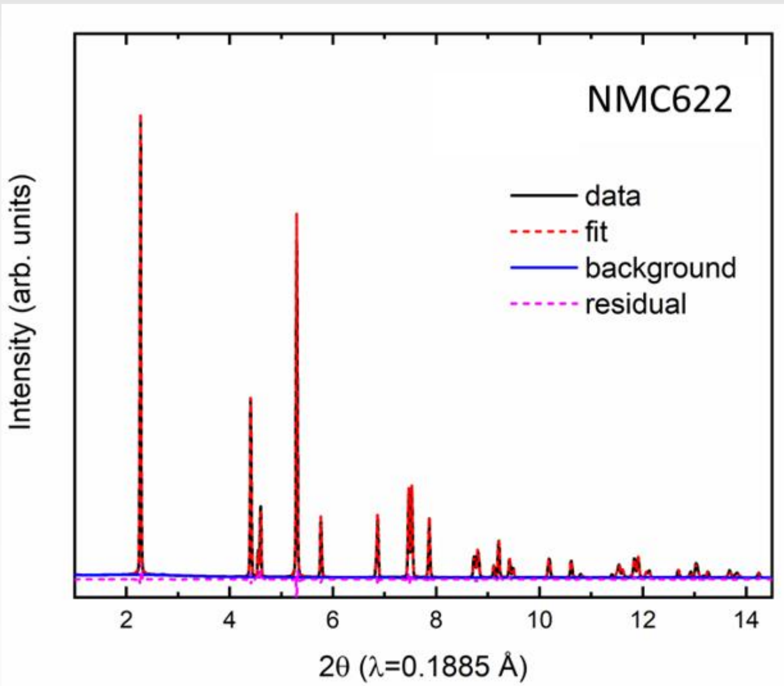


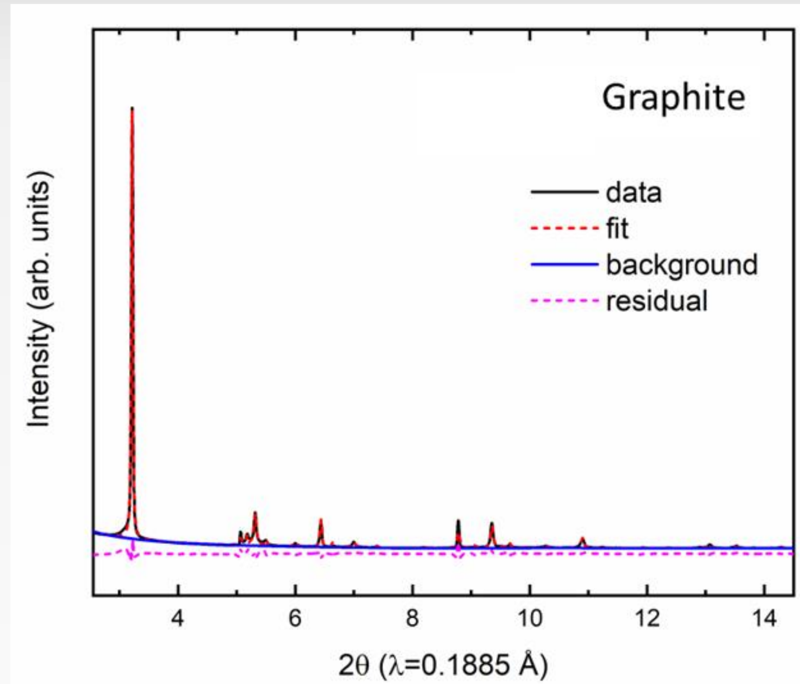


NMC 622: Average particle size: 11± 4 µm; BET surface area: 0.3 m^2/g

Graphite: Average particle size: 7 ± 1 µm ; BET surface area: 1.9 m^2/g

Technical Progress – Electrode Material Characterization



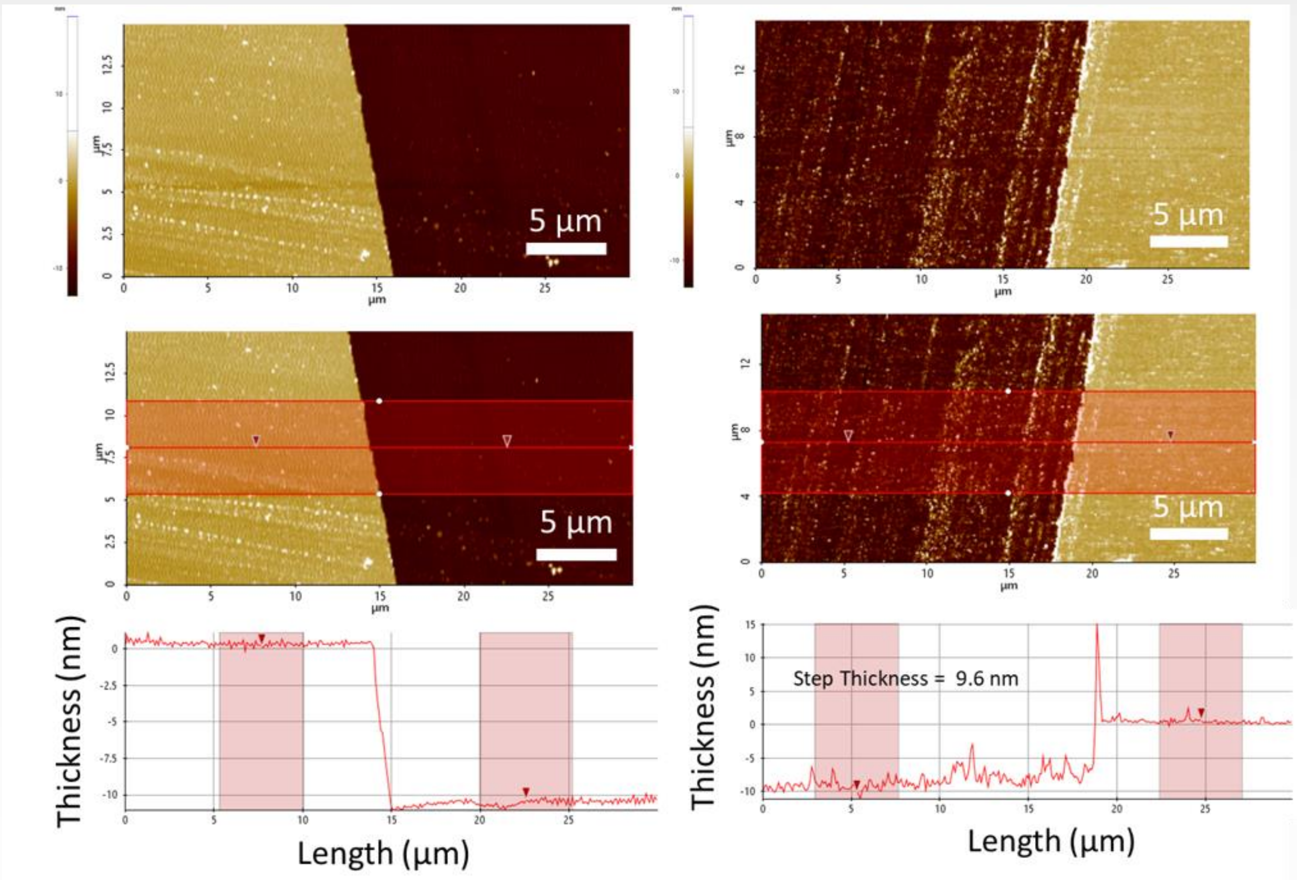


- NMC 622: Indexed to $R\bar{3}m$ space group; no impurity phases present. Cation disorder: 2.1% for pristine material. Elemental composition from ICP-OES: $Li_{1.01}Ni_{0.61}Mn_{0.20}Co_{0.19}$.

- Graphite: Mixture of hexagonal (Space group $P6_3/mmc$ space group, 73%) and rhombohedral ($R\bar{3}m$ space group, 27%) phases; no impurity phases present.

Technical Progress – Surface Treatment and Thickness Determination by AFM

M film M’ film

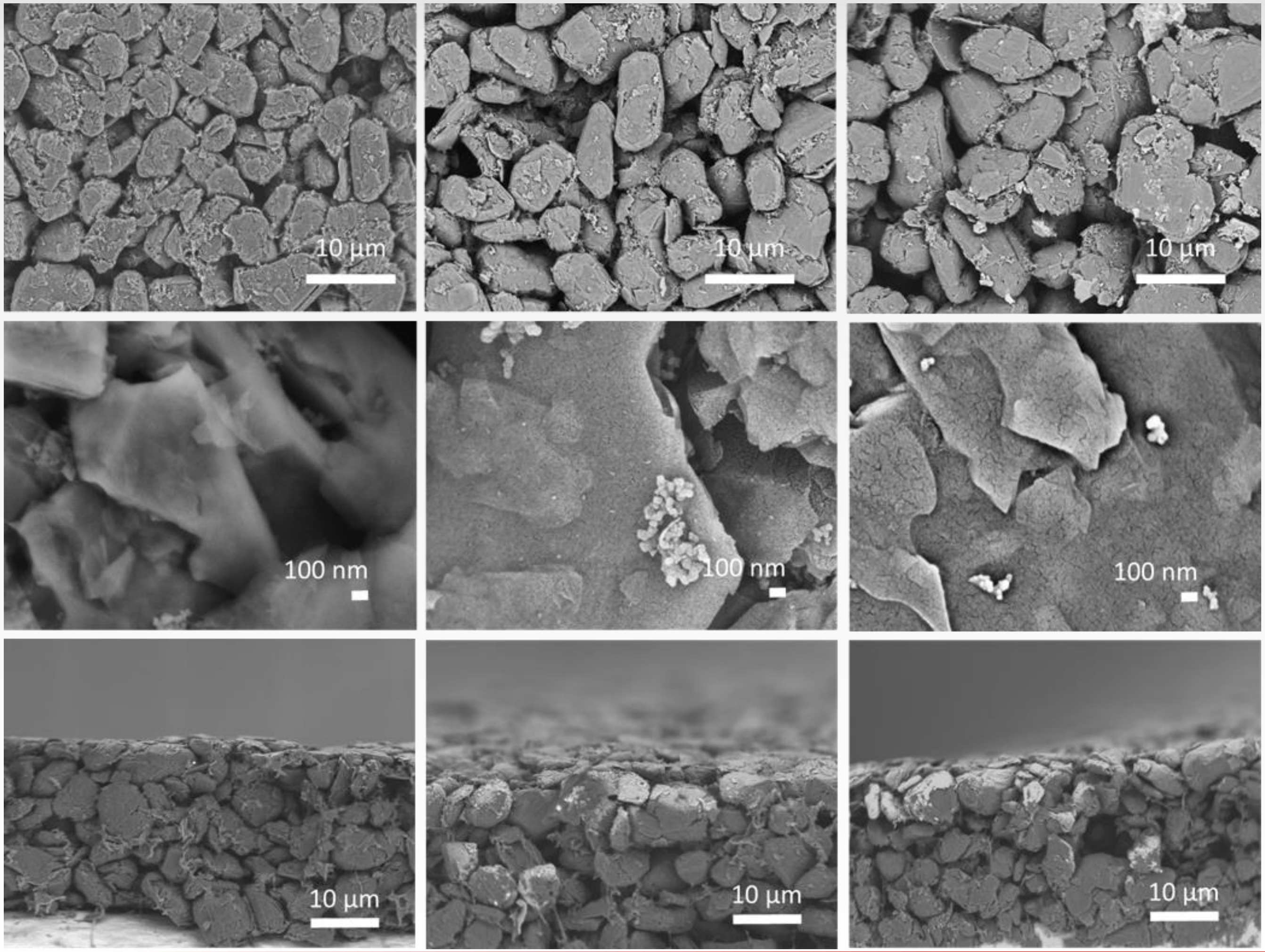


- Thicknesses of the deposited films were verified via non-contact atomic force microscopy (AFM) analyses of silicon wafers

- Average thicknesses were determined to be 10.2 ± 0.6 nm (n= 10) and 9.7 ± 0.7 nm (n= 10)

Technical Progress – SEM of Surface Treated Graphite

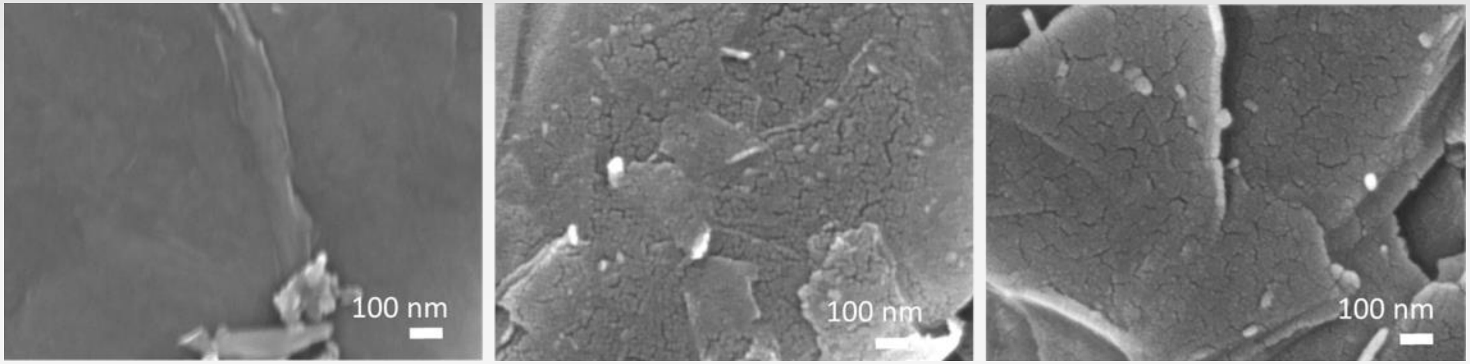
graphite | 10 nm M - graphite | 10 nm M' - graphite



- Surface films are concentrated at the electrode surface with partial coverage between adjacent graphite particles.

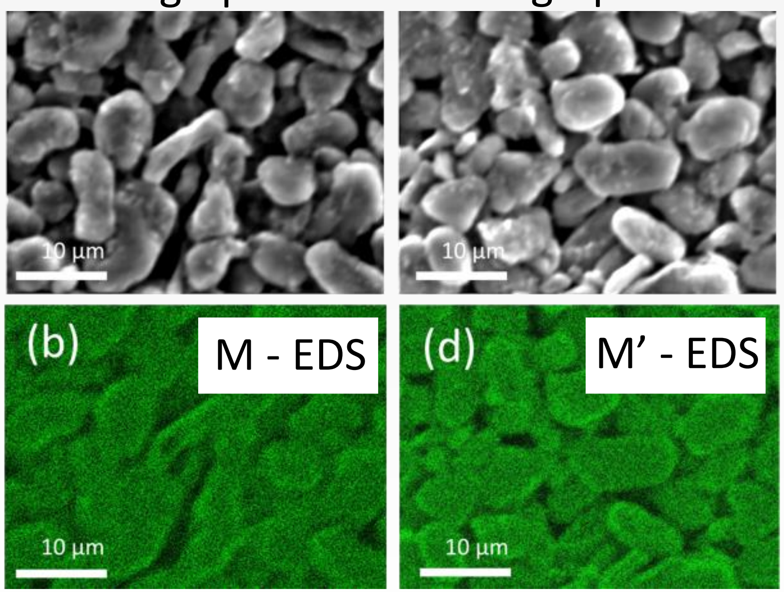
Technical Progress – SEM of Surface films on Graphite

graphite | M - graphite | M'- graphite



EDS Mapping

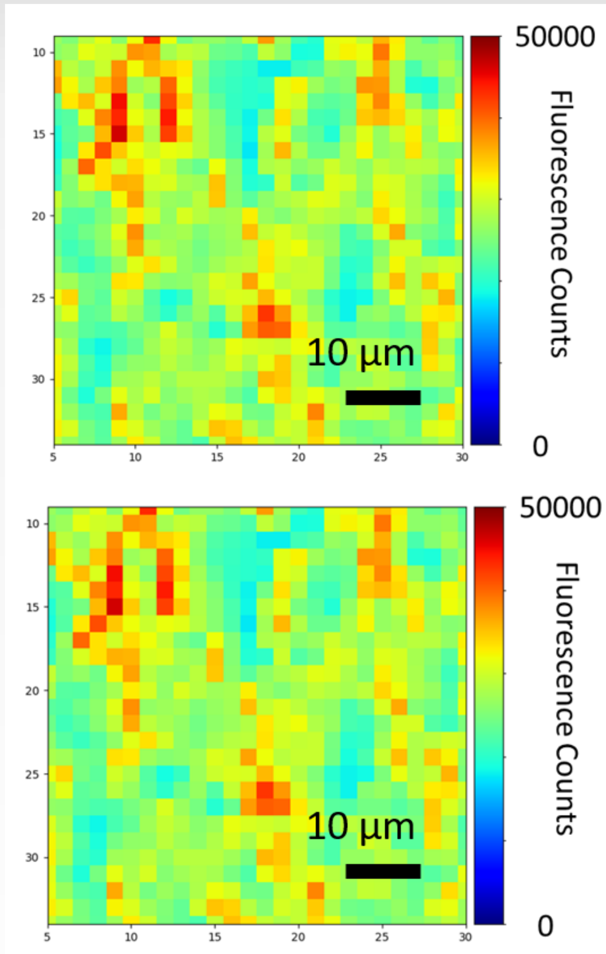
M - graphite | M' - graphite



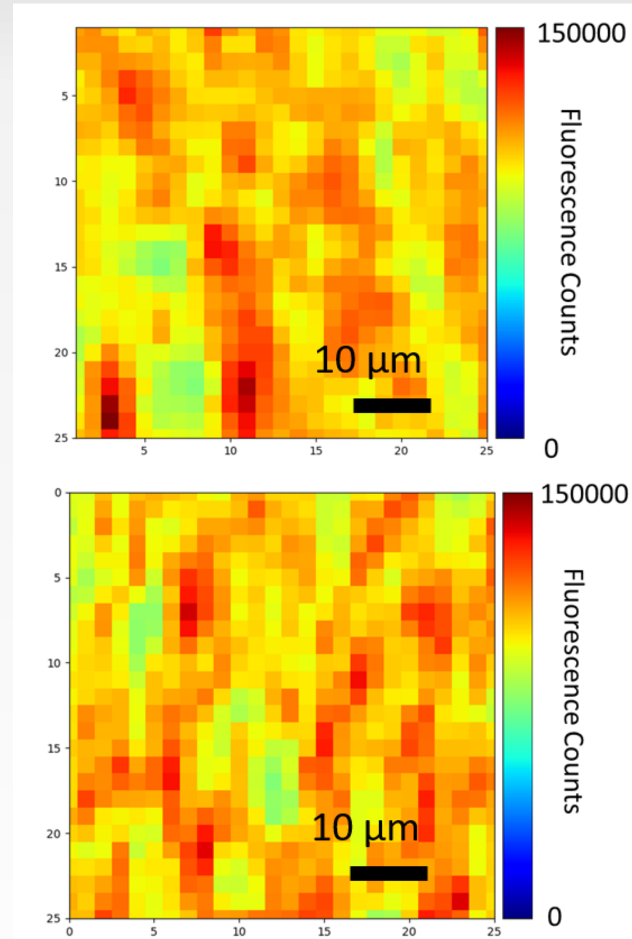
- SEM – SE: surface texture of the treated electrodes can be visualized as small cracks.
- EDS maps of the electrodes indicate good uniformity of the deposited layers on the electrode surfaces.

Technical Progress – XRF Maps

M XRF maps



M’ XRF maps

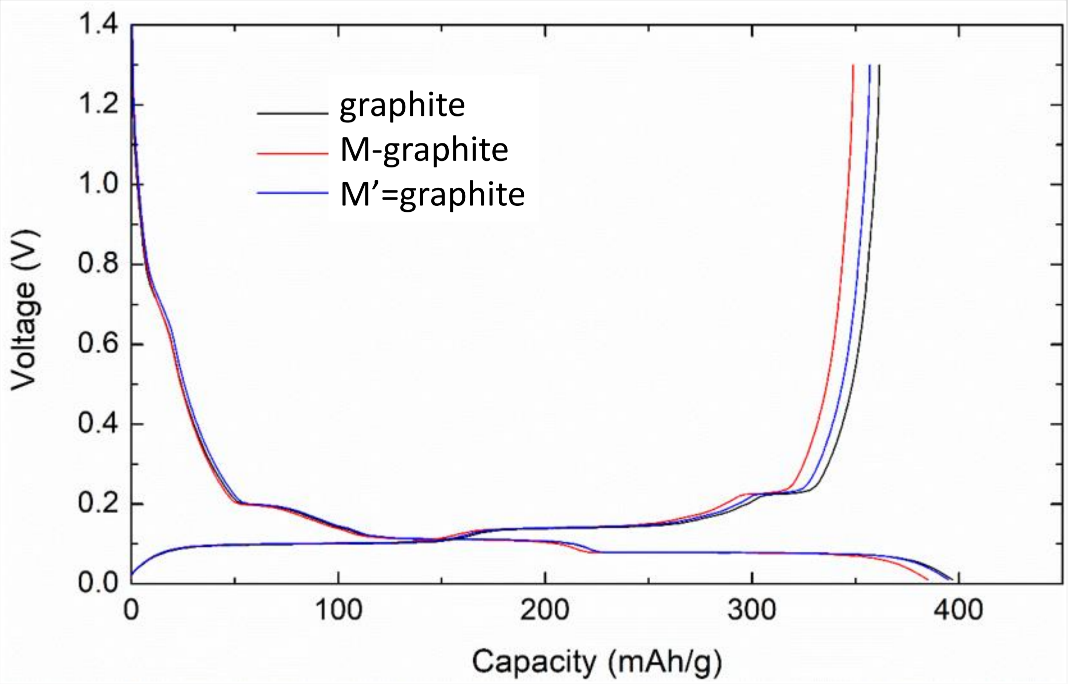


undischarged

after formation

For M and M’, XANES analyses was also completed, with LCF fits

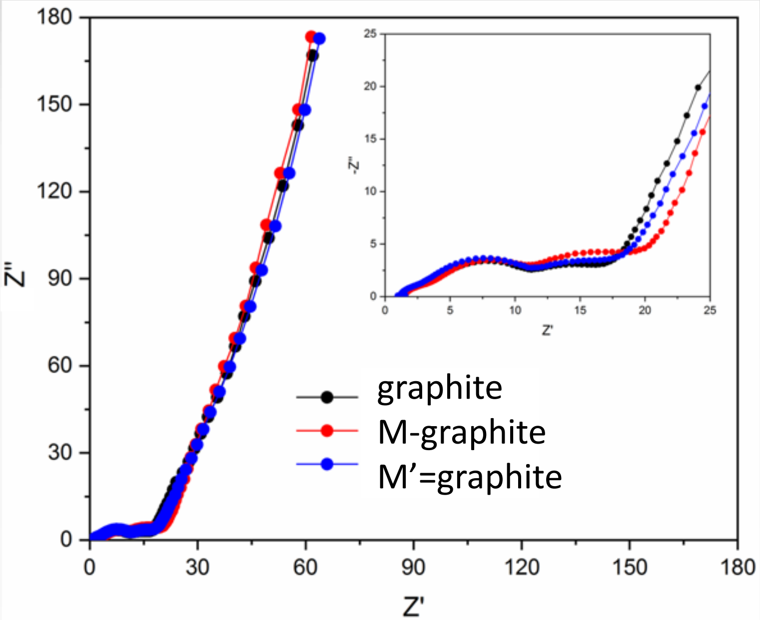
Technical Accomplishments and Progress – Formation Cycling of untreated and treated graphite cells

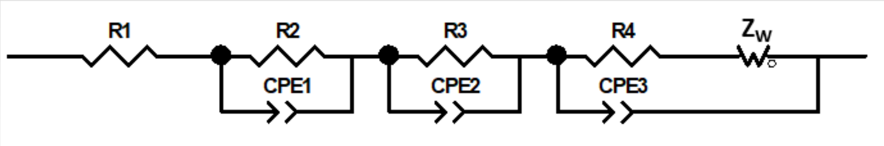


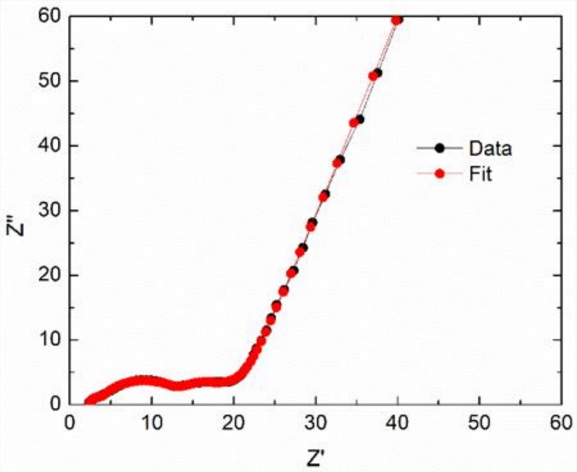
- Electrode loading: 4.5 mg cm^{-2}; porosity = 30 – 35%
- 4 cycles, C/10, 0.01 – 1.3 V
- Irreversible Capacity is within error for all three electrode types

Electrode	1st discharge (mAh/g)	1st charge (mAh/g)	Irreversible Capacity (mAh/g)
graphite	399 ± 5	362 ± 5	37 ± 7
M-graphite	388 ± 5	353 ± 5	35 ± 8
M'-graphite	394 ± 4	356 ± 5	38 ± 6

Technical Accomplishments and Progress – Impedance of untreated and treated graphite cells



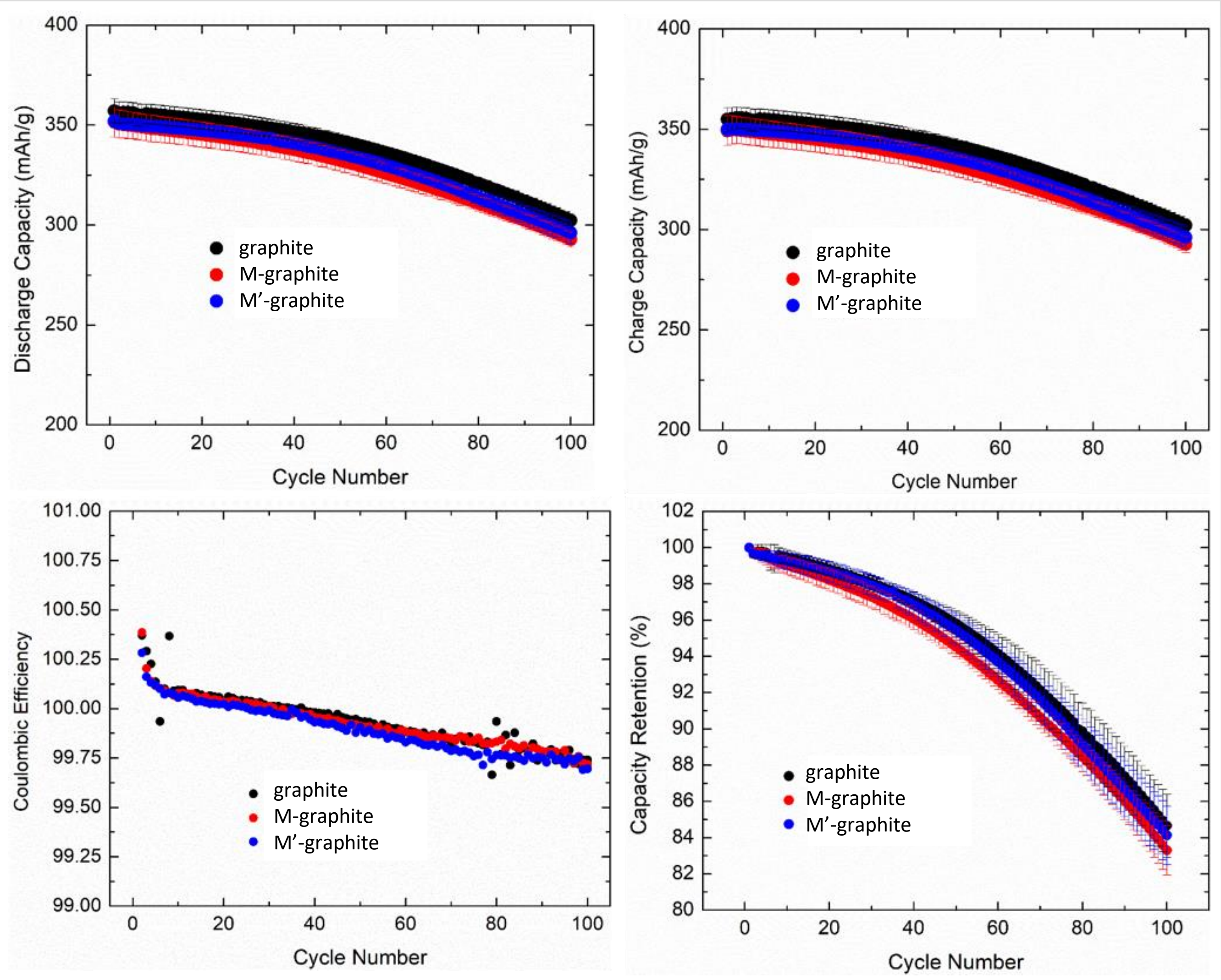




Electrode	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)	R_4 (Ω)	$Z_{w,R}$ (Ω)	$Z_{w,T}$ (Ω)	$Z_{w,P}$
graphite	1.5 ± 0.3	1.9 ± 0.3	8.1 ± 0.5	1.5 ± 0.3	15 ± 1	0.73 ± 0.07	0.399 ± 0.002
M-graphite	1.5 ± 0.5	2.6 ± 0.4	8.5 ± 0.7	1.5 ± 0.1	18 ± 2	0.9 ± 0.1	0.402 ± 0.003
M'-graphite	1.7 ± 0.5	1.9 ± 0.1	7.8 ± 0.8	1.2 ± 0.2	16 ± 2	0.77 ± 0.06	0.403 ± 0.004

- Impedance measured after formation cycling: 100 mHz – 100 kHz
- Impedance values are within error for all three electrode types (n=3 per group)

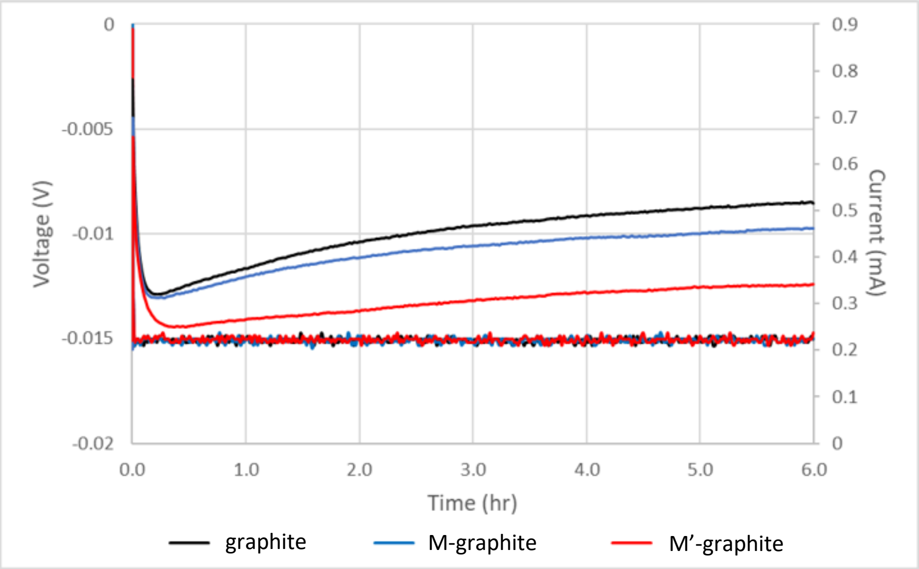
Technical Progress – Functional Capacity of untreated and treated graphite cells



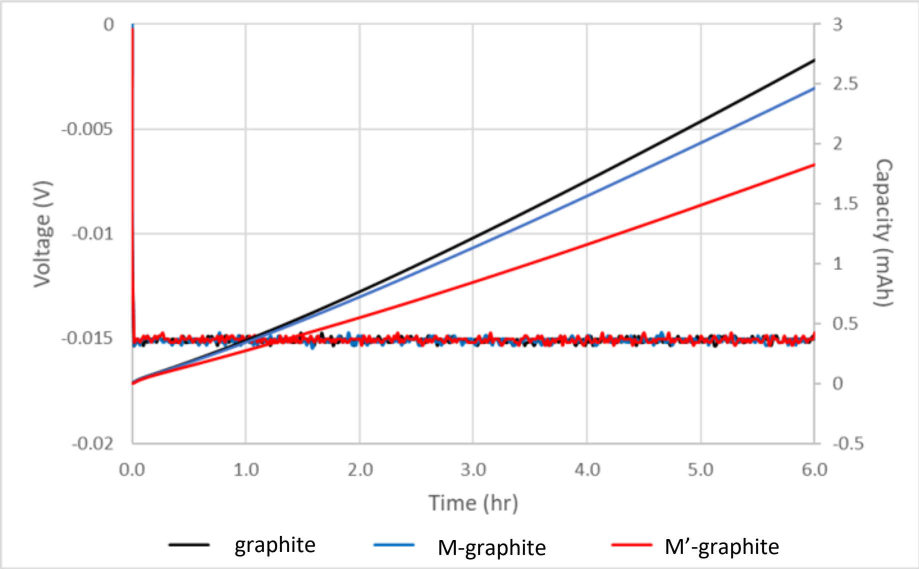
- Electrode loading: 4.5 mg cm^{-2}; porosity = 30 – 35%
- C/2 rate; 0.01 – 1.3 V
- Capacity retention of untreated and treated graphite cells all within error of each other (n=3 per group)

Technical Progress – Comparison of Li Plating on untreated and treated graphite cells

Current vs. Time



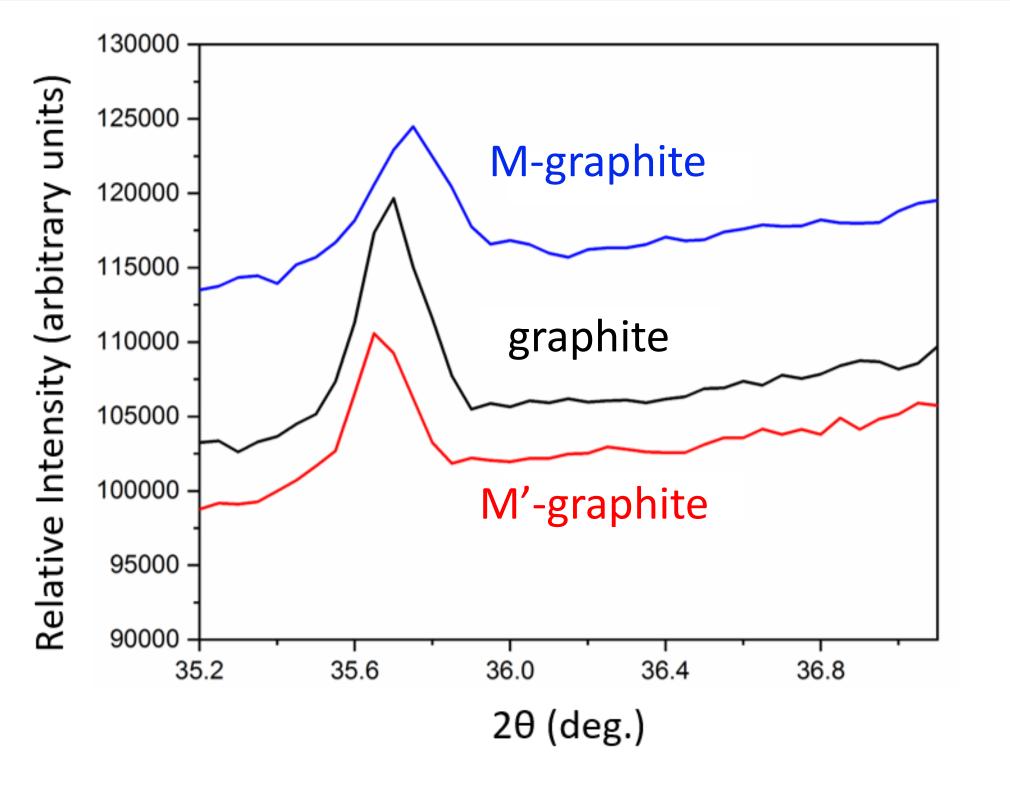
Capacity vs. Time



- Fully lithiated electrodes of each type were held at -15 mV for 6 hours
- Surface treated electrodes have reduced Li plating current relative to uncoated graphite

Technical Accomplishments and Progress – Li Quantification by XRD

Li (110) peak, after -15 mV hold (6 hr)



XRD peak fitting results

Electrode Type	Li(110) Peak Area	Li(110) Peak Intensity
graphite	1650	7790
M-graphite	1130	4300
M’-graphite	760	2770

- A lower quantity of Li metal deposited on M-graphite and M’-graphite relative to uncoated graphite electrodes after 6 hour -15 mV hold

Collaborations; Remaining Challenges and Barriers

Collaborations

- User proposal systems actively used for interaction with Brookhaven National Laboratory (National Synchrotron Light Source II, Center for Functional Nanomaterials) for metal film deposition and characterization.
- Brookhaven National Laboratory leads cell characterization efforts

Challenges and Barriers

- Characterize Li deposition under different conditions (charge rates, graphite polarization voltages)
- Optimize surface treatments to minimize Li plating while maximizing cell rate capability
- Evaluate fast charging capability vs. control cells with uncoated graphite electrodes

Proposed Future Research

- **Go/ No-Go:** Demonstrate full cell utilizing surface treated electrode capable of 50 cycles at C/2 charge rate and capacity retention >80% of control cells
- Prepare and characterize surface treated graphite electrodes at three different thicknesses
- Perform Li plating experiments with quantification of deposited lithium by XRD
- Optimize surface treatment type and thickness and evaluate fast charging capability vs. control cells with uncoated graphite electrodes

Any proposed work is subject to change based on funding levels

Summary

Program is on schedule.

- Electrode materials have been obtained and characterized.
- Surface treatments of graphite electrodes has been accomplished with thicknesses verified by AFM.
- Coverage homogeneity of the surface treatments on graphite has been characterized by SEM (BSE, SE), EDS mapping, and XRF mapping.
- Oxidation state of the deposited films before and after formation has been characterized by XPS, XAS.
- Functional capacity of treated and untreated graphite electrodes has been characterized by galvanostatic cycling.
- Initial Li plating deposition experiments show reduced Li plating on surface treated graphite compared to untreated graphite electrodes.
- Development of full cells utilizing surface treated electrodes is on track.